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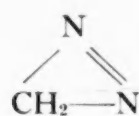
Rochester 4, N. Y.

## "Meso-Ionic" Compounds

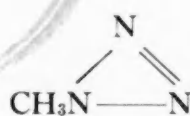
By EDWARD M. CRANE\*

It is nowadays generally conceded that many, if not most, organic compounds cannot be completely characterized by a single covalent structure, or indeed by any number of covalent structures. The abundance of evidence for ionic reactions leads one to the conclusion that if the structures of such compounds are not ionic, they must at least show a strong predisposition toward ionization under certain circumstances. A good formula must concur with the facts, and the theory of resonance provides an attractive means to that end (1).

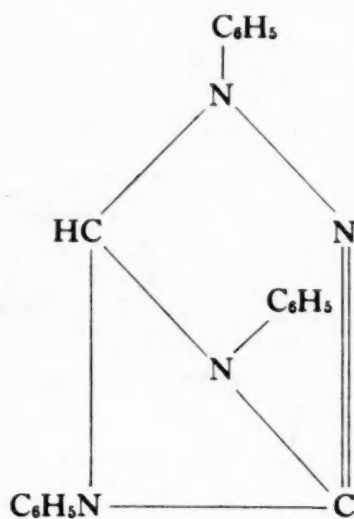
There are some compounds for which all possible covalent structures are extremely improbable. (In connection with a statement of this kind, it must be remembered that in a submicroscopic world holding an enormous number of individuals the word "improbable" has quantitative significance. Improbable structures do contribute to the hybrid which constitutes the molecule being formulated, but they do not contribute much.) The most prominent examples all have three- or four-membered rings in their classical formulations: diazomethane I, triazomethane II, "nitron" III, the *endothiothiadiazolines* IV and V, the *endoiminothiadiazoline* VI, and N-phenylsydnone VII:



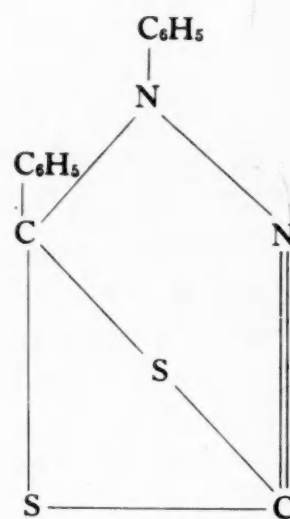
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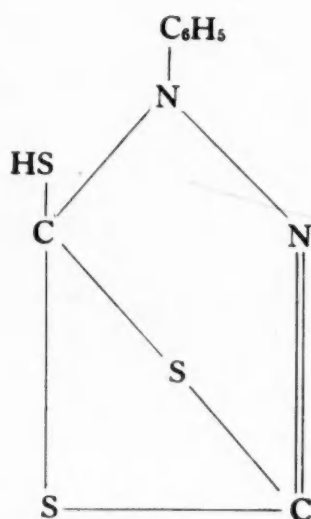
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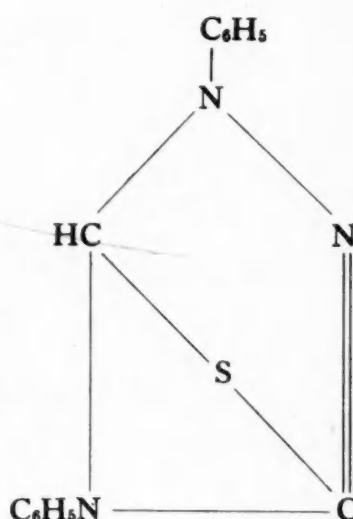
III



IV

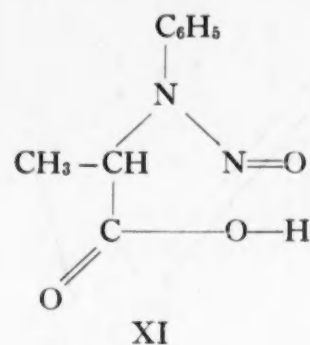
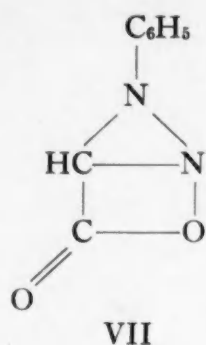


V



VI

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The development of a more rational formula for the sydnone is a recent one. The name of this class of compounds is derived from that of the University of Sydney, where in 1935 J. Campbell Earl reported (2) the attempt to prepare from N-nitroso-N-phenylglycine VIII a substance IX analogous to the acetyl gamma-lactone shown below it.

Unexpectedly, the crystalline product corresponded not to Formula IX but rather to VII. Water was not replaced by acetic acid but rather lost altogether. Deacetylation to X, analogous to the well-known enol-lactones, was discredited because "the formation of a double bond is not possible" (2).

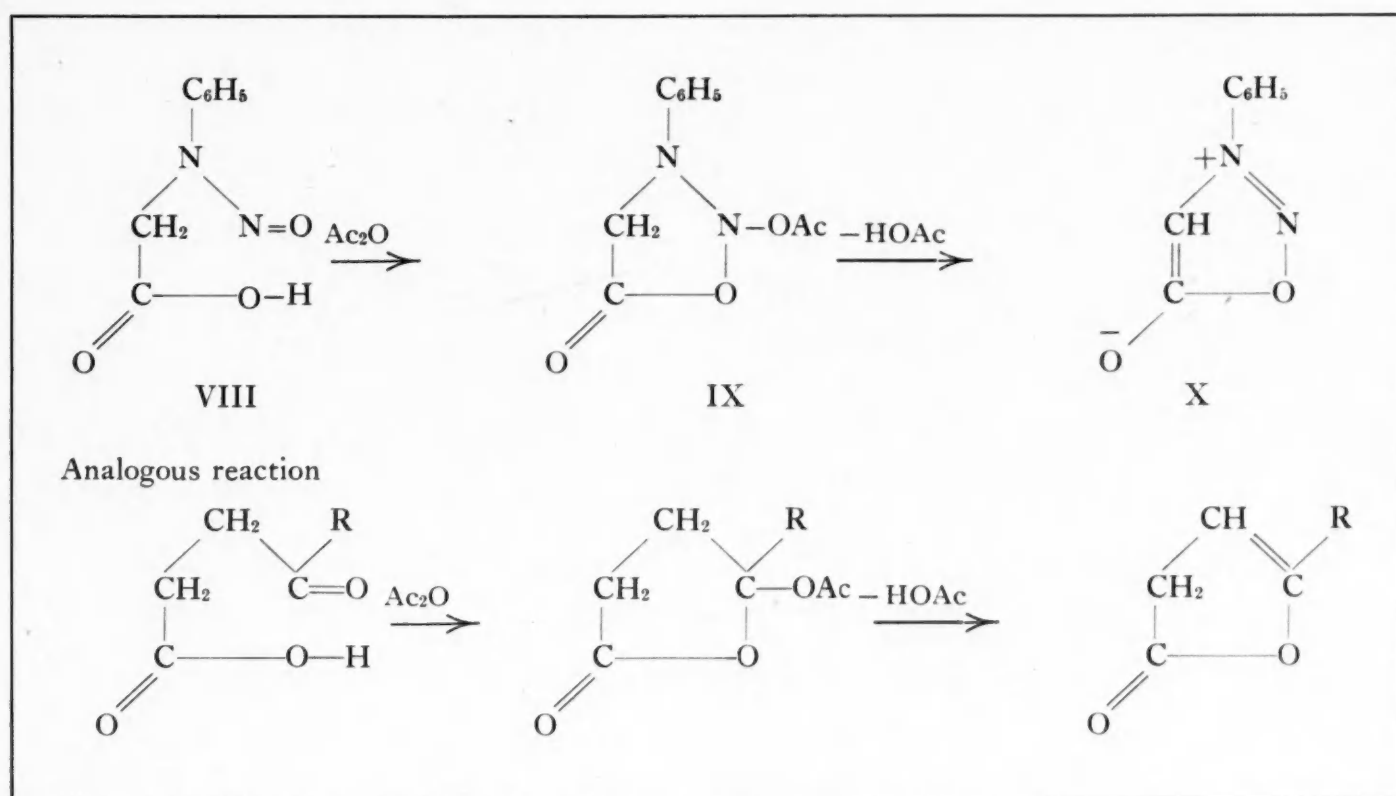
Compound XI, with only two available hydrogens to lose, behaved identically.

The reaction was peculiar to nitroso compounds, and it was reasonable to as-

sume that the nitroso oxygen was the one lost. The admirably simple and useful rules of "lasso" chemistry led inexorably to Formula VII.

Molecular weight determination and a negative Liebermann nitroso reaction agreed with Formula VII. Strong acid broke down the product to phenylhydrazine, formic acid, and carbon dioxide. Alkali regenerated the nitroso acid (VIII). In 1935, then, Formula VII was proposed without qualification.

But in the same year, after a quarter century of doubt and debate, the structure of diazomethane was established (3) as that of Formula XIV (which is not, however, universally accepted without reservation even now—see reference 4). A similar structure (XV) was fully confirmed (5) for the organic triazo compounds. And three years later Formulas III-VI for the reagent "nitron"

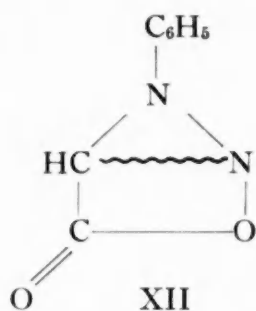


and its congeners were displaced (6) by Formulas XVI-XIX.

Eight years later still, Professor Earl had accumulated (7) a number of variously substituted sydnones and a commendable skepticism. In 1946, Formula VII was "tentative," and as such attracted a good deal of attention.

First in the field was Wilson Baker of the University of Bristol (8) with the suggestion that only charge separation forms such as X contribute to N-phenyl sydnone. But close behind him, Kenner and Mackay of the College of Technology, Manchester (9) reported that optically active N-nitroso-N-phenyl alanine (XI) gives an inactive sydnone, and that N-phenyl sydnone is instantly brominated, like an enol. They stated flatly that the structure is that of Formula X.

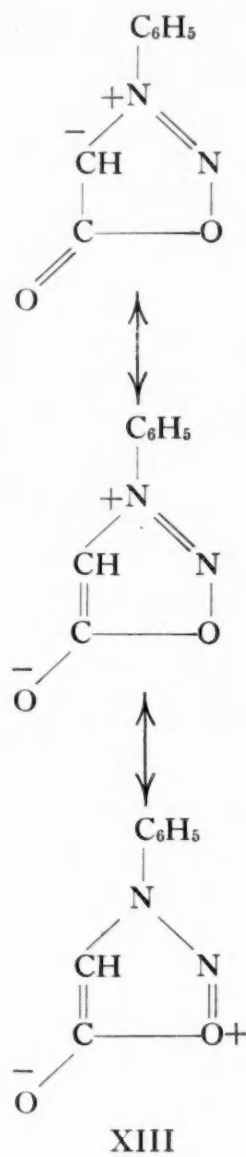
Another note from Professor Earl appeared at the same time (10). He too had found that an optically active nitroso acid yielded an inactive sydnone, but remarked that the sydnones have no obvious dipolar characteristics. They are indeed soluble in benzene. He conceded a point with Formula XII. The wavy line represents a "partly formed" covalent bond.



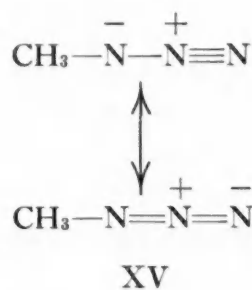
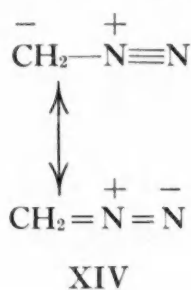
Professor Baker subsequently published (14) some evidence in favor of his earlier suggestion. Important points are the relative stability of a wide variety of aromatic and aliphatic sydnones compared with compounds known to be beta-lactones, and their ultraviolet absorption spectra which indicate a considerable degree of conjugation or aromaticity.

The crucial experiment was reported simultaneously by Professor Earl (11,

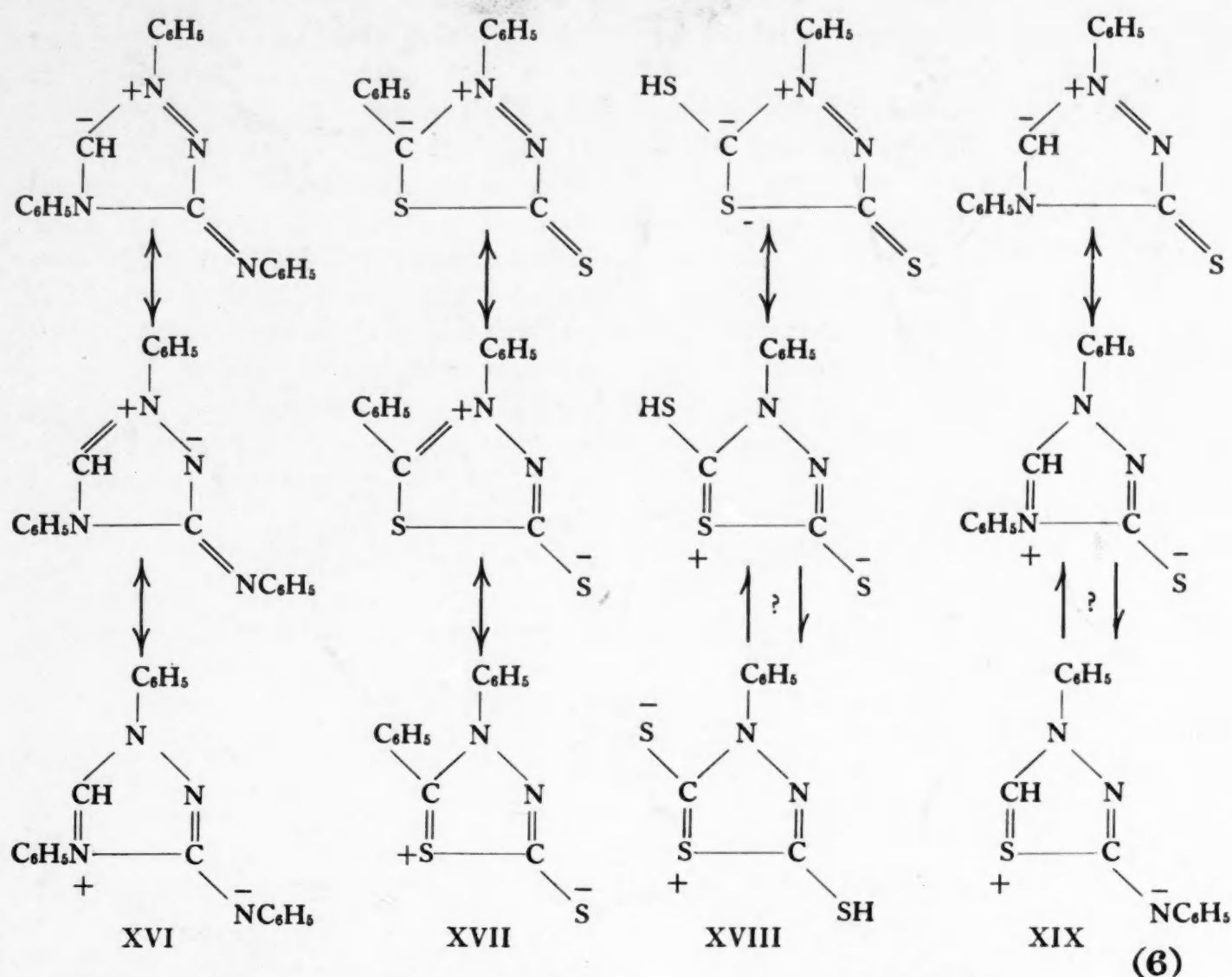
13) and, with the support of Professor Baker (12), by Hill and Sutton of Oxford University (15). The dipole moments of the known sydnones are so large, and so directed, that there can no longer be any doubt that Formula X, or its somewhat expanded form XIII, is as good a representation of the molecule as can be made. The formal charges, or coordinate covalences, define extremes bounding the real hybrid. Doubtless there are scores of other contributors, but a few must represent the many.



Similarly, Formulas I-VI stand amended as XIV-XIX.







Professor Baker (14, 16) proposes for such compounds the term "meso-ionic." There is no harm in it provided the reader remembers that the sydnones and other compounds so classed are in no way different from any compounds with important resonance stabilization. Assigning definite positions to electrons is only a convenience in writing and using formulas. But the description "meso-ionic" must not be abused. It is applied specifically to a compound which cannot "be satisfactorily represented either by a single covalent form, or as a hybrid of a few covalent forms, e.g., benzene and naphthalene, or as a hybrid of covalent and ionic forms, e.g., the amides" (14). The conventional amide formulation  $\text{>N}-\overset{\overset{|}{\text{O}}}{\underset{+}{\text{C}}}=\text{O}$  implies in large measure also  $\text{>}\overset{+}{\text{N}}=\overset{\overset{|}{\text{O}}}{\underset{-}{\text{C}}}-\text{O}$ . Hence even a six-membered bis-lactam can be assigned a covalent formula without misapprehension, and does not deserve the appellation "meso-ionic" (17).

#### References

- (1) Remick, "Electronic Interpretations of Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, 1949.
- (2) Earl and Mackney, *J. Chem. Soc.*, 1935, 899.
- (3) Boersch, *Monats.*, 65, 311 (1935).
- (4) Eistert, in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, New York, 1948, p. 513.
- (5) Brockway and Pauling, *Proc. Nat. Acad. Sci.*, 19, 860 (1933); Knaggs, *Proc. Roy. Soc.*, 150A, 576 (1935); Hughes, *J. Chem. Phys.*, 3, 1 (1935).
- (6) Schönberg, *J. Chem. Soc.*, 1938, 824; Jensen and Friediger, *Chem. Abstr.*, 39, 2068 (1945).
- (7) Eade and Earl, *J. Chem. Soc.*, 1946, 591.
- (8) Baker and Ollis, *Nature*, 158, 703 (1946).
- (9) Kenner and Mackay, *Nature*, 158, 909 (1946).
- (10) Earl, *Nature*, 158, 910 (1946).
- (11) Earl, Leake, and LeFevre, *Nature*, 160, 366 (1947).
- (12) Baker *et al*, *Nature*, 160, 366 (1947).
- (13) Earl, Leake and LeFevre, *J. Chem. Soc.*, 1948, 2269.
- (14) Baker, Ollis, and Poole, *J. Chem. Soc.*, 1949, 307.
- (15) Hill and Sutton, *J. Chem. Soc.*, 1949, 746.
- (16) Baker, *Endeavour*, 9, 35 (1950).
- (17) Brown and Hammick, *J. Chem. Soc.*, 1950, 628.